

# Influence of Packing of the Reactants and Products in Solution on the Volume Parameters of the Diels–Alder Reaction

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**Abstract**—The possible causes of a dramatic difference in the volume parameters (by up to 15–20 cm<sup>3</sup> mol<sup>-1</sup>) of the Diels–Alder reactions involving bulky and small reactants are discussed. The partial molar volumes of anthracene and 9,10-dihydroanthracene and the heats of their solution in six solvents were determined.

It is known [1–3] that the activation ( $\Delta V^\ddagger$ ) and reaction ( $\Delta V_0$ ) volumes determined from the dependences of the rate ( $k$ ) and equilibrium ( $K$ ) constants on the external pressure [Eqs. (1), (2)] furnish additional information on the structure of the activated complex whose volume ( $V^\ddagger$ ) can be calculated with Eq. (3).

$$(\partial \ln k / \partial p)_T = -1/RT(\partial \Delta G / \partial p)_T = -\Delta V^\ddagger / RT, \quad (1)$$

$$(\partial \ln K / \partial p)_T = -1/RT(\partial \Delta G_0 / \partial p)_T = -\Delta V_0 / RT, \quad (2)$$

$$V^\ddagger = V_{\text{react}} + \Delta V^\ddagger. \quad (3)$$

Here  $R$  is the universal gas constant;  $T$ , temperature;  $\Delta G^\ddagger$  and  $\Delta G_0$ , activation and reaction Gibbs energies, respectively; and  $V_{\text{react}}$ , total molar volume of the reactants.

The relationship between the molar volumes of the activated complex, reactants, and reaction products, and also the quantity  $\theta = \Delta V^\ddagger / \Delta V_0$  allow better understanding of the reaction mechanism and the influence exerted by the reactants, catalysts, products, and reaction medium on the volume parameters of reactions [1–5].

It is still unclear why the volume parameters of the nonpolar Diels–Alder reaction can dramatically change in a series of related reactants. As the molar volumes of diene–dienophile pairs increase, the absolute values of the volume parameters of the reactions considerably decrease [3–6]. For example, in the reactions of dienophiles with cyclopentadiene or alkylbutadienes, the activation and reaction volumes range from –35 to –40 cm<sup>3</sup> mol<sup>-1</sup>, whereas in the reactions with anthracene derivatives these quantities are from –20 to –25 cm<sup>3</sup> mol<sup>-1</sup>. There are no grounds to assume changes in the reaction mechanism in the series

of related reactants. The significant difference in the volume parameters of the Diels–Alder reaction reflects the fact that the packing coefficients  $\eta$  ( $\eta = V_{\text{W}}/V$ , where  $V_{\text{W}}$  is the molar van der Waals volume) of bulkier reactants increase less significantly in going to the activated complex and then to the adduct. On the other hand, the packing coefficient is only a general characteristic of a substance in solution, bearing no information on factors responsible for changes in the partial molar volumes in going from one reactant to another or, for given reactants, from one solvent to another.

Revealing the effect of solvation on variation of the molar volumes of the reactants, activated complex, and reaction products is one of the key steps in revealing the causes of changes in the reaction rates and equilibria at elevated pressures. The volume of a dilute solution can be described by Eq. (4).

$$V = V_{\text{A}}N_{\text{A}} + V_{\text{S}}N_{\text{S}} + (V_{\text{S}}^* - V_{\text{S}})qN_{\text{A}}. \quad (4)$$

Here  $V_{\text{A}}$ ,  $V_{\text{S}}$ , and  $V_{\text{S}}^*$  are the molar volumes of the solute, solvent in the bulk, and solvent in the solvation sphere;  $q$  is the number of solvent molecules in the solvation sphere; and  $N_{\text{A}}$  and  $N_{\text{S}}$  are the amounts (moles) of the solute and solvent, respectively. Hence, the partial molar volume of a solute ( $V_{\text{A}}$ ) in a dilute solution is given by

$$\partial V / \partial N_{\text{A}} = V_{\text{A}} + q(V_{\text{S}}^* - V_{\text{S}}). \quad (5)$$

In the absence of specific interactions in solution ( $V_{\text{S}}^* - V_{\text{S}} = 0$ ), the partial molar volume of a solute can be calculated from the solution density by the additive scheme of bond or atom increments [7, 8]. If the solute–solvent interaction is strong, the additivity is disturbed because of a large change in the solvent

volume on its passing from the bulk to the solvation shell. In such cases, the calculated partial molar volumes can be even negative [9]. Apparently, the problem persists in going to infinitely dilute solutions also. Since separate experimental determination of  $q(V_S^* - V_S)$  and  $V_A$  is impossible, all changes in these quantities are assigned to the solute molar volume ( $V_A$ ).

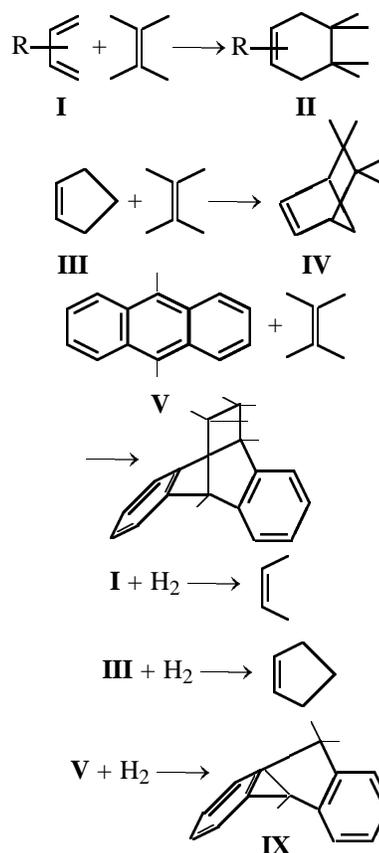
The experimental values of the activation or reaction volume reflect changes in the volume of the whole reaction system in going to the activation complex or reaction products. Therefore, the difference between the partial molar volumes of the reactants and products always corresponds to the true reaction volume in the given system. The activation volume can be calculated only from the dependence of the reaction rate constant on the external pressure [Eq. (1)], whereas the reaction volume can be determined either from the dependence of the equilibrium constant on the external pressure [Eq. (2)] or independently from the difference between the partial molar volumes of the products and reactants. Thus, it becomes possible to check the validity of the volume parameters determined with Eq. (2).

The partial volume of the solute can considerably change in cases when the solvent–solvent and solvent–solute interaction energies differ considerably. It was shown [6, 10] that in the case of specific solute–solvent interactions the enthalpy of solvation clearly correlates with the change in the partial molar volume. However, as far as we compare the activation and reaction volumes for the Diels–Alder reactions involving the same dienophiles and different dienes (alkylbutadienes and cyclopentadiene, on the one hand, and substituted anthracenes, on the other hand), there are no specific interactions of the dienes with the solvent. Therefore, the large difference in the volume parameters of these reactions ( $\delta V$  15–20 cm<sup>3</sup> mol<sup>-1</sup>) should be accounted for by features of variation of the molar volumes in going from the reactants to the activated complex and then to the adduct, rather than by specific interactions of the reaction participants with the medium (see scheme). It should be noted that the difference between the van der Waals volumes of the products and reactants ( $\Delta V_W$ ) in Diels–Alder reactions involving various reactants is always approximately constant,  $-10 \pm 2$  cm<sup>3</sup> mol<sup>-1</sup>. This means that the experimentally determined activation and reaction volumes for the Diels–Alder reactions involving alkylbutadienes **I** or cyclopentadiene **III** (from  $-35$  to  $-40$  cm<sup>3</sup> mol<sup>-1</sup>) include a contribution from a decrease in the volume of intermolecular cavities, ranging from  $-25$  to  $-30$  cm<sup>3</sup> mol<sup>-1</sup>. In the processes involving substituted anthracenes **V**, the contribution from changes in the intermolecular and, possibly, intramo-

lecular cavities is considerably smaller: from  $-10$  to  $-15$  cm<sup>3</sup> mol<sup>-1</sup>.

This difference may be caused by two factors: either by a smaller change in the volume of intermolecular cavities in the process involving more closely packed molecules of anthracene **V** in solution or by increased partial molar volume of reaction product **VI** because of the presence of a void between the benzene ring planes in the adduct, inaccessible for solvation.

In this work, we checked whether solvation of adduct **VI** is hindered. If the internal void of **VI** is inaccessible for solvation, then the partial molar volume of the adduct will be increased by the volume of this void. The volume inaccessible for the solvent molecules should be 15–20 cm<sup>3</sup> mol<sup>-1</sup>. Since the difference in the volumes ( $\Delta V_0$ ) is observed in the reactions of these dienes involving common nucleophiles, our hypothesis can be verified by comparing the molar volumes of the sterically accessible structures (**II**, **IV** and **VII**, **VIII**) with those of the structures whose solvation may be hindered (**VI**, **IX**). Note that, in going from a planar anthracene molecule **V** to adduct **VI** or to 9,10-dihydroanthracene **IX**, the same internal void is formed. If the internal void of **IX** is, indeed, inaccessible for solvation, the volumes of hydrogenation of **I** and **III** should also differ from the volume of hydrogenation of **V** by 15–20 cm<sup>3</sup> mol<sup>-1</sup>.



**Table 1.** Partial molar volumes ( $V$ ,  $\text{cm}^3 \text{mol}^{-1}$ ), packing coefficients ( $\eta = V_{\text{W}}/V$ ), and enthalpies of solution ( $\Delta H_{\text{sol}}$ ,  $\text{kJ mol}^{-1}$ ) of anthracene and 9,10-dihydroanthracene and the volumes of hydrogenation ( $\Delta V_{\text{hydr}}$ ,  $\text{cm}^3 \text{mol}^{-1}$ ) of anthracene to 9,10-dihydroanthracene

Solvent	Anthracene			9,10-Dihydroanthracene			$\Delta V_{\text{hydr}}$
	$V$	$\eta$	$\Delta H_{\text{sol}}$	$V$	$\eta$	$\Delta H_{\text{sol}}$	
Toluene	158.0±0.2	0.696	24.8±0.8	163.8±0.1	0.693	19.5±0.3	5.8±0.3
1,4-Dioxane	159.5±0.1	0.690	22.7±0.5	165.6±0.2	0.685	19.2±0.3	6.1±0.3
Ethyl acetate	153.7±0.5	0.715	25.1±0.2	160.9±0.1	0.705	20.0±0.6	7.2±0.6
Cyclohexanone	159.8±0.5	0.688	20.6±0.5	165.0±0.2	0.688	17.4±0.3	5.2±0.7
Acetonitrile	158.2±0.2	0.695	28.0±0.3	164.8±0.2	0.689	25.1±0.3	6.6±0.4
Chloroform	157.5±0.2	0.698	20.8±0.3	163.6±0.1	0.694	15.5±0.3	6.1±0.3

To check this assumption, we determined the partial molar volumes of anthracene and 9,10-dihydroanthracene in certain solvents (Table 1).

The choice of **V** and **IX** is also justified by the fact that these structures only slightly differ in the composition and molar weight; therefore, if both structures are accessible for solvation, the packing coefficients for them should be similar.

The solvent effect on the partial molar volumes of anthracene and 9,10-dihydroanthracene appeared to be small (up to 5–6  $\text{cm}^3 \text{mol}^{-1}$ ) but noticeably exceeding the measurement error. This fact indicates that the packing of the solvent molecules in the solvation shell around the solute can noticeably differ from the packing of the solvent molecules in the bulk. However, the solvent effects on the molar volumes of **V** and **IX** are approximately proportional ( $r$  0.969). The solvent effects on the enthalpies of solution (Table 1) of **V** and **IX** are significant (up to 10  $\text{kJ mol}^{-1}$ ) and also approximately proportional ( $r$  0.934); however, the variations in the enthalpy of solution and molar volume mutually correlate neither for anthracene **V** ( $r$  0.374) nor for dihydroanthracene **IX** ( $r$  0.076). This means that variations in the energy of nonspecific solvation and partial molar volume are determined by different factors. This conclusion is consistent with data of [6].

The observed and van der Waals molar volumes of a series of alkanes, alkenes, and cycloalkanes are listed in Table 2. These data allow us to construct a series of correlations showing how the molar volume depends on the structure and size of the molecules:

$$V(\text{C}_n\text{H}_{2n+2}) = (35.10 \pm 0.45) + (15.96 \pm 0.06)n; \quad (6)$$

$$r \ 0.99997,$$

$$V_{\text{W}}(\text{C}_n\text{H}_{2n+2}) = (7.63 \pm 0.15) + (10.36 \pm 0.02)n; \quad (7)$$

$$r \ 0.99999.$$

$$V_{\text{W}}(\text{C}_n\text{H}_{2n+2})$$

$$= (-15.15 \pm 0.41) + (0.6492 \pm 0.0026)V(\text{C}_n\text{H}_{2n+2}); \quad (8)$$

$$r \ 0.99997,$$

$$V(\text{C}_n\text{H}_{2n}) = (28.63 \pm 0.52) + (16.07 \pm 0.06)n; \quad r \ 0.99996, \quad (9)$$

$$V_{\text{W}}(\text{C}_n\text{H}_{2n}) = (5.28 \pm 0.20) + (10.31 \pm 0.02)n; \quad (10)$$

$$r \ 0.99999,$$

$$V_{\text{W}}(\text{C}_n\text{H}_{2n}) = (-13.09 \pm 0.31) + (0.6415 \pm 0.0019)V(\text{C}_n\text{H}_{2n});$$

$$r \ 0.99998, \quad (11)$$

$$V(\text{cyclo-C}_n\text{H}_{2n}) = (24.41 \pm 0.98) + (13.86 \pm 0.12)n; \quad (12)$$

$$r \ 0.99980,$$

$$V_{\text{W}}(\text{cyclo-C}_n\text{H}_{2n}) = (1.74 \pm 0.43) + (10.17 \pm 0.06)n; \quad (13)$$

$$r \ 0.99994,$$

$$V_{\text{W}}(\text{cyclo-C}_n\text{H}_{2n}) = (-17.12 \pm 0.91)$$

$$+ (0.7421 \pm 0.0070)V(\text{cyclo-C}_n\text{H}_{2n}); \quad r \ 0.99994. \quad (14)$$

Here  $n$  is the number of carbon atoms in the molecules of alkenes, alkanes, and cycloalkanes. Direct calculation of the volume of the  $\text{CH}_2$  group from the molar volume of any alkane  $\text{C}_n\text{H}_{2n+2}$  is impossible, because the volume of the  $\text{CH}_3$  group is unknown also. The difference between the molar volumes of the adjacent homologs in the series of alkanes [ $15.96 \pm 0.06$ , Eq. (6)] or alkenes [ $16.07 \pm 0.06$ , Eq. (9)] includes not only the molar volume of the  $\text{CH}_2$  group but also changes in the volume of intermolecular cavities. This assumption is confirmed by the fact that the molar volume of the  $\text{CH}_2$  group in cycloalkanes [ $V_{\text{W}}(\text{cyclo-C}_n\text{H}_{2n})/n$ ] appreciably decreases (18.8, 18.0, 17.3, 16.8, 16.5, 16.3, and 15.9  $\text{cm}^3 \text{mol}^{-1}$ ) in going from *cyclo-C*<sub>5</sub>H<sub>10</sub> to *cyclo-C*<sub>12</sub>H<sub>24</sub>, with the difference between the molar volumes of the adjacent homologs in the cycloalkane series being approximately constant [ $13.86 \pm 0.12$ , Eq. (12)]. On the other hand,

**Table 2.** Molar ( $V$ ) and van der Waals ( $V_W$ ) volumes ( $\text{cm}^3 \text{mol}^{-1}$ ) of a series of hydrocarbons, their packing coefficients ( $\eta = V_W/V$ ), and volumes of cyclization ( $\Delta V_{\text{cycl}}$ ) and hydrogenation ( $\Delta V_{\text{hydr}}$ ,  $\text{cm}^3 \text{mol}^{-1}$ ) at  $20^\circ\text{C}$ 

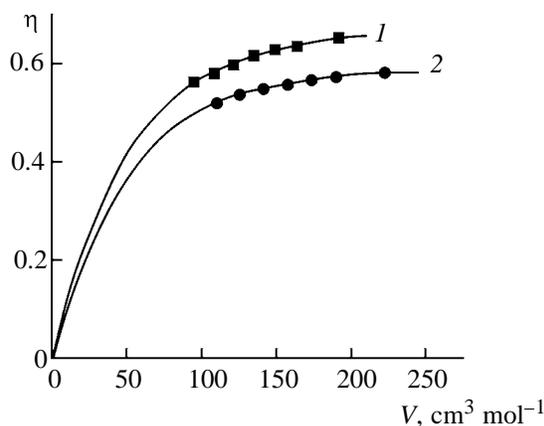
No.	Compound	$V^a$	$V_W$	$V_W/V$	$\Delta V_{\text{cycl}}^b$	$\Delta V_{\text{hydr}}^b$
1	Pentane	115.2	59.4	0.516		5.7 (1–3)
2	Cyclopentane	94.1	52.9	0.562	–15.4 (2–3)	5.9 (2–4)
3	1-Pentene	109.5	56.9	0.520		
4	Cyclopentene	88.2	50.1	0.568		
5	Hexane	130.7	69.9	0.535		5.7 (5–7)
6	Cyclohexane	108.1	62.7	0.580	–16.9 (6–7)	6.8 (6–8)
7	1-Hexene	125.0	67.3	0.538		
8	Cyclohexene	101.3	59.7	0.589		6.0 (8–9)
9	1,3-Cyclohexadiene	95.3	56.2	0.590	–16.4 (9–11)	6.7 (8–10)
10	1,4-Cyclohexadiene	94.6	56.9	0.602		5.7 (10–13)
11	1,3,5-Hexatriene (Z)	111.7	59.7	0.535		
12	1,3-Hexadien-5-yne	100.1	57.4	0.573		
13	Benzene	88.9	54.0	0.607	–11.2 (13–12)	
14	Heptane	146.6	80.1	0.546		4.4 (15–17)
15	Cycloheptane	121.3	72.7	0.599	–19.6 (15–16)	5.7 (14–16)
16	1-Heptene	140.9	77.3	0.549		
17	Cycloheptene	116.9	69.7	0.596		
18	Octane	162.6	90.5	0.557		5.6 (18–20)
19	Cyclooctane	134.4	83.0	0.618	–22.6 (19–20)	4.4 (19–21)
20	1-Octene	157.0	87.6	0.558		
21	cis-Cyclooctene	130.0	79.8	0.614		
22	Nonane	178.7	100.8	0.564		5.8 (22–24)
23	Cyclononane	148.3	93.3	0.629	–24.6 (23–24)	5.0 (23–25)
24	1-Nonene	172.9	98.0	0.567		
25	cis-Cyclononene	143.3	90.1	0.629		
26	Decane	194.9	111.3	0.571		5.6 (26–28)
27	Cyclodecane	163.3	103.7	0.635	–26.0 (27–28)	5.7 (27–29)
28	1-Decene	189.3	108.4	0.573		5.0 (28–30)
29	cis-Cyclodecene	157.6	100.7	0.639		
30	1,9-Decadiene	184.3	104.9	0.569		
31	cis-Decalin	154.2	96.7	0.627	–30.1 (31–30)	
32	1-Dodecene	221.9	129.1	0.582	–28.1 (32–7–7) <sup>c</sup>	
33	Dodecane	227.5	131.8	0.579	–28.2 (33–5–7) <sup>c</sup>	5.6 (33–32)
34	Cyclododecane	191.3	124.4	0.650	–30.6 (34–32)	

<sup>a</sup> The molar volumes of the compounds were calculated from their densities [11]. <sup>b</sup> In parentheses are the numbers of compounds whose molar volumes were taken to calculate  $\Delta V_{\text{cycl}}$  and  $\Delta V_{\text{hydr}}$  as the differences. <sup>c</sup> Volumes of linear annelation.

the van der Waals volumes  $V_W(\text{CH}_2)$  in the series of acyclic [ $10.36 \pm 0.02$ , Eq. (7);  $10.31 \pm 0.02$ , Eq. (10)] and cyclic [ $10.17 \pm 0.06$ , Eq. (13)] alkanes nicely agree with the  $[V_W(\text{cyclo-C}_n\text{H}_{2n})/n]$  values calculated for each cycloalkane ( $10.42 \pm 0.06 \text{ cm}^3 \text{mol}^{-1}$ ). All these data are consistent with the presumed increase in the packing coefficient ( $\eta = V_W/V$ , Table 2) of molecules in a liquid with an increase in their molar weight and volume. Similar conclusions were also obtained when comparing the  $\eta$  values and entropies of formation of cycloalkanes [12]. The limiting values of  $\eta$  for alkenes [ $0.6415 \pm 0.0019$ , Eq. (11)] are appreciably low-

er than for cycloalkanes [ $0.7421 \pm 0.0070$ , Eq. (14)] (Fig. 1).

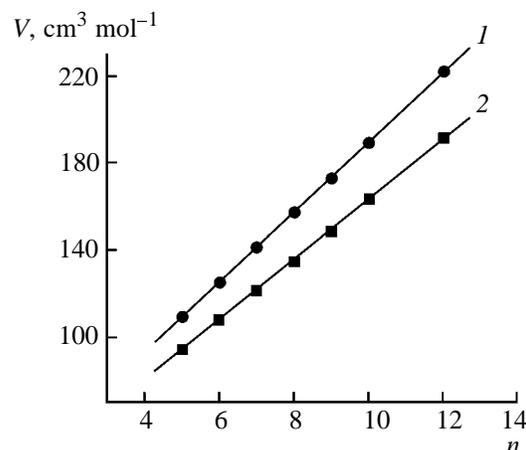
These data show that the volume of the same monomolecular process of intramolecular cyclization ( $\Delta V_{\text{cycl}}$ ) by the scheme of ene addition, equal to the difference between the molar volumes of the cycloalkane and alkene, is not constant (Fig. 2) and becomes more negative (from  $-15.4$  to  $-30.6 \text{ cm}^3 \text{mol}^{-1}$ , Table 2) with increasing molecular size. This trend is consistent with the fact that cyclization with formation of a new C–C bond is accompanied by a loss of the



**Fig. 1.** Correlation of the packing coefficients  $\eta$  of (1) cycloalkanes and (2) alkenes with their molar volumes  $V$  at 20°C.

free rotation of groups in the alkene and, correspondingly, by a decrease in the relative volume of intermolecular cavities; in large molecules, these differences in volumes are more significant (Fig. 2). On the other hand, the difference in the van der Waals volumes ( $\Delta V_{W, cycl}$ ) for these pairs of compounds ( $C_nH_{2n} \rightarrow cyclo-C_nH_{2n}$ ), firstly, is considerably smaller than  $\Delta V_{0, cycl}$ , secondly, is constant throughout the series ( $\Delta V_W = -4.6 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ , Table 2), and, thirdly, is close to the half of  $\Delta V_W$  for the Diels–Alder reaction ( $-10 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$ ) in which two new C–C bonds are formed. As noted in [12], the volume of cyclization of alkenes to cycloalkanes does not correlate with the enthalpy and entropy of the process. The volume of bimolecular transformation of two 1-pentene molecules into 1-decene is  $-29.7 \text{ cm}^3 \text{ mol}^{-1}$ , and into cyclodecane,  $-55.7 \text{ cm}^3 \text{ mol}^{-1}$ . The related transformations of two 1-hexene molecules are accompanied by volume changes of  $-28.1$  and  $-58.7 \text{ cm}^3 \text{ mol}^{-1}$ , respectively (Table 2). These data are consistent with the assumption [13] that the observed volume parameters of reactions consist of the contributions made by changes in the van der Waals volumes and volumes of intermolecular cavities.

The packing coefficients of the corresponding acyclic pairs  $C_nH_{2n}-C_nH_{2n+2}$  differ insignificantly [Eqs. (8), (11)]; as a result, the hydrogenation volumes are approximately constant ( $\Delta V_{hydr} 5.7 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$  without taking into account the molar volume of hydrogen, Table 2). For the same reason, the volumes of hydrogenation of cycloalkenes to cycloalkanes are also approximately constant:  $5.6 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$  (Table 2). In this case,  $\Delta V_{W, hydr}$  is also smaller than  $\Delta V_{hydr}$  and



**Fig. 2.** Correlation of the molar volumes  $V$  of (1) alkenes and (2) cycloalkanes  $C_nH_{2n}$  at 20°C with the number of hydrogen atoms  $n$ .

approximately constant ( $2.8 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ ) for all the pairs of compounds under consideration (Table 2).

Similar packing coefficients of anthracene and 9,10-dihydroanthracene in any solvent of the examined series ( $\eta_V/\eta_{IX} 1.007 \pm 0.003$ , Table 1) indicate that there is no void in **IX** inaccessible for solvation. This conclusion is additionally confirmed by the fact that the mean volumes of hydrogenation (without taking into account the molar volume of hydrogen, Table 2) of alkenes accessible for solvation to alkanes ( $5.7 \pm 0.1$ ) and of cycloalkenes to cycloalkanes ( $5.6 \pm 0.7$ ) only slightly differ from the mean volume of hydrogenation of anthracene to dihydroanthracene ( $6.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ , Table 1). These data show that the structural voids in dihydroanthracene **IX** and hence in Diels–Alder adduct **VI** derived from anthracene are accessible for solvation with the examined solvents and hence cannot be responsible for the dramatic differences in the volumes of the Diels–Alder reaction. Thus, significant differences in the volume parameters of the nonpolar Diels–Alder reaction involving reactants of different size are primarily caused by different extent of changes in the volume of intermolecular, rather than intramolecular, voids in the course of the reaction. We can estimate the limiting volumes of the Diels–Alder reaction involving reactants of different size. With the small reactants, butadiene ( $V 83.2 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\eta 0.538$ ) and ethylene ( $V 59.9 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\eta 0.425$ ) [15], the volume of the reaction yielding cyclohexene ( $V 101.3 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\eta 0.589$ , Table 2) is  $-41.8 \text{ cm}^3 \text{ mol}^{-1}$ . If for large molecules of the reactants and products we assume the same limiting value of  $\eta$ , 0.75 [Eq. (14)], we obtain

considerably smaller (in the absolute value) reaction volume, from  $-13$  to  $-15 \text{ cm}^3 \text{ mol}^{-1}$ . The contribution from a decrease in the intermolecular voids to the reaction volume will be  $-32 \text{ cm}^3 \text{ mol}^{-1}$  for the former reaction and from  $-3$  to  $-5 \text{ cm}^3 \text{ mol}^{-1}$  for the reaction involving bulky reactants. Since a decrease in the partial molar volume under applied pressure is primarily due to the contraction of voids, the reactants with a low packing coefficient should show stronger deviation from linear dependences (1) and (2) for Diels–Alder reactions.

## EXPERIMENTAL

The chemicals (Aldrich) were purified by column chromatography ( $\text{Al}_2\text{O}_3$ ), eluent benzene–hexane, 1 : 3. The solvents were purified by standard procedures [16].

The partial molar volumes of the reactants in dilute solutions were calculated from the solutions densities, which, in turn, were determined with a resonating tube (A. PAAR, DMA 602) at  $25^\circ\text{C}$ . The accuracy of density measurements was  $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$ . The temperature was maintained constant to within  $\pm(1-2) \times 10^{-3}^\circ\text{C}$ . The apparent molar volume ( $\varphi_A$ ) can be calculated from the density of a single solution [Eq. (15)] or from data for a series of solutions, using the dependence of  $(1000 + m_A M_A)/d$  on  $m_A$  [Eq. (16)]:

$$\varphi_A = 1000(d_0 - d)/m_A d d_0 + M_A/d, \quad (15)$$

$$(1000 + m_A M_A)/d = 1000/d_0 + m_A \varphi_A. \quad (16)$$

Here  $d$  and  $d_0$  are the solution and solvent densities;  $m_A$ , molal concentration of the solution; and  $M_A$ , molar weight of the solute. Relationship (16) shows how the apparent molar volume of the solute  $\varphi_A$  depends on its concentration. In the examined concentration range (up to  $0.01 \text{ mol kg}^{-1}$ ), no significant deviations from (16) were observed ( $r > 0.9999$ ). The measurement results are given in Table 1.

The enthalpies of solution of **V** and **IX** in a series of solvents were determined calorimetrically [17]. The solute concentrations did not exceed  $5 \times 10^{-3} \text{ M}$ .

The van der Waals volumes of the compounds were calculated by the MOLVOL program submitted by Prof. F.-G. Klarner (Essen, Germany).

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